PRELIMINARY DESIGN OF PARAXYLENE PLANT
USING SELECTIVE TOLUENE DISPROPORTIONATION PROCESS
CAPACITY OF 400,000 TONS/ YEAR

by:

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CHEMICAL ENGINEERING DEPARTMENT

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HALAMAN PERSETUJUAN

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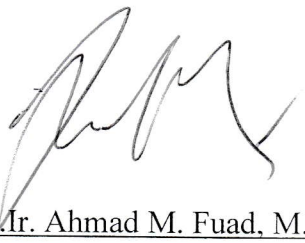

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HALAMAN PENGESAHAN

PREMINARY DESIGN PARAXYLENE
***DISPROPORSIONASI TOLUEN* PROCESS**
CAPACITY OF 400.000 TON/TAHUN

OLEH

DELTA MUTIARA
D 500 122006

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Fakultas Teknik
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Pada hari Senin, 06 Februari 2017
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Abstract

Paraxylene dihasilkan melalui proses *selective toluene disproportionation* dengan katalis zeolit ZSM-5. Reaksi berlangsung dalam fase gas pada suhu 450°C dan tekanan 30 atm. Pemurnian paraxylene dilakukan dengan proses pemisahan distilasi kritalisasi sehingga didapatkan kemurnian 99,9%. Pabrik *paraxylene* dirancang dengan kapasitas produksi 400.000 ton/tahun. Proses membutuhkan 695,205 ton/tahun toluena dan 1,214 ton/tahun hidrogen digunakan sebagai bahan baku. Pabrk ini direncanakan dibangun di kawasan industri di Cilegon, Banten pada tahun 2020 dengan luas tanah 3,800 m^2 dan mempekerjakan 166 karyawan. Unit pendukung pabrik ini terdiri dari unit penyedia air sebesar 968,907 kg/jam yang diolah dari Sungai Ciujung, unit penyediaan uap jenuh sebesar 296,130,095 kJ/jam, unit penyediaan listrik sebesar 998 kW, unit penyediaan bahan bakar sebesar 236 liter/jam, unit penyediaan udara instrument sebesar 50 m^3/jam dan unit penyediaan amonia sebesar 3.252 kg/jam amonia. Jumlah modal kerja Rp.162,007,798,698. Analisis ekonomi menunjukkan bahwa persen return of investasi (ROI) sebelum pajak adalah 86% dan setelah pajak adalah 64%. *Pay out time* (POT) sebelum pajak adalah 1 tahun dan *pay out time* (POT) setelah pajak adalah 1,3 tahun. *Break even point* (BEP) pada 43,54% kapasitas produksi, *shut down point* (SDP) adalah sebesar 27% kapasitas produksi, dan d*iscounted cash flow* (DCF) sebesar 25%. Dari data hasil analisis kelayakan dapat disimpulkan bahwa pabrik tersebut menguntungkan dan layak untuk didirikan.

Kata kunci : *Paraxylene, selective toluene disproportionation,* katalis zeolit ZSM-5.

Abstract

Paraxylene is produced through selective toluene disproportionation process with zeolite catalyst ZSM-5. The reaction takes place in the gas phase at temperature of 450°C and pressure of 30 atm. Paraxylene purification through separation process by distillation and crystallization to obtain purity of 99.9%. Plant is designed with production capacity of 400,000 tons/year. 695,205 tons/year of toluene and 1,214 tons/year of hydrogen are used as raw material. The plant is planned to establish in Cilegon industrial area, Banten in 2020 with land area 3,800 m^2 and hire 166 employees. Supporting unit of the plant consist of water supply as much as 968,907 kg/hour which are processed from Ciujung River, provision 296,130,095 kJ/hour of saturated steam, provision 998 kW of electricity, provision 236 liters/hour of diesel fuel, provision 50 m^3/hour of instrumentation air and provision 3,252 kg/hour of ammonia. Amount of working capital is Rp.162,007,798,698. The economic analysis shows that percent return on investment (ROI) before tax is 86% and after tax is 64%. Pay out time (POT) before tax is 1 year and pay out time (POT) after tax is 1.3 year. Break even point (BEP) at 43.54 % capacity, Shut down point (SDP) is amounted at 27% capacity,

and Discounted cash flow (DCF) is 25%. From data results of feasibility analysis can be concluded that the plant is profitable and feasible to be established.

Keywords: Paraxylene, selective toluene disproportionation, zeolite catalyst ZSM-5.

1. INTRODUCTION

1.1 Background

Paraxylene also called 1.4 dimethyl benzene is classified into aromatic compounds. Paraxylene is an intermediate product which is used widely in chemical industry. This material can be further processed into several kinds of end products. Paraxylene is primarily used as raw material in the manufacture of terephthalic acid (TPA) and dimethyl-terephthalate (DMT). TPA and DMT are used to manufacture polyethylene terephthalate (PET) saturated polyester polymers.

1.2 Design capacity

Determination of paraxylene plant capacity can be viewed from severalconsiderations, among others:

a. Projection of Paraxylene Demand in Indonesia

By using the least squares method y = bx + a, it can be estimated paraxylene import demand (kg/year). It can be estimate demand of paraxylene in 2020 will reach 1,008,946,107 kg/year .

b. Capacity of Existing Plant

In determining capacity plant, it can be seen from capacity of plant that has been established. Paraxylene plant in Indonesia which has been operated is Pertamina UP IV Cilacap with production capacity 270,000 ton/year and started operating since 1990.

Due to above consideration , it is possible to build this plant with capacity 400,000 ton/year to cover domestic demand in Indonesia.

1.3 Literature review

1.3.1 Kinds of Process

Two principal methods for producing xylenes are catalytic reforming and toluene disproportination

a. Mixed xylene Production via Reforming

In catalytic reforming, a low octane naptha cut (typically a straight run or hydrocracked naphta) is converted into high octane aromatics, including benzene, toluene and mixed xylenes. Aromatic are separated from reformate using a solvent such as diethylene glycol and sulfolane and then stripped from the solvent.distilation is then used to separate BTX (benzene, tolunen, xylene) into its components. The amount of xylenes contained in catalytic reformate depends on the fraction and type of crude oil, the reformer operating condition and the catalyst used. Typically ranging from 18 to 33 vol% of the reformate. (kirk othmer vol 4)

b. Xylenes production via toluene transalkylation and disproportionation.

The toluene disproportionation is defined as the reaction of 2 mol of tolunene to produced 1 mol of xylene and 1 mol of benzene. Toluene transalkyation is defined as the reaction of toluenen with c9 or higher aromatics to produce xylenes .

There are several commercial processes that produce xylenes via disproportionation or transalkylation.

1). UOP's Tatoray and PX-Plus

In this process, toluene or a mixture of toluene and C9+ aromatics are reacted to form primariy xylenes and benzene. The catalyst is designet TA-4. It has high per pass conversion and good stability. Yields to xylenes are reported to be over 97%. The pelleted catalyst is used in fixed bed reactor in the presence of hydrogen. Typical operating condition are: 350-530°C, 1-5 Mpa (10-50 atm) and H2/hydrocarbon ratio of 5-12:1. Toluene per pass conversion can be increased by increasing pressure or temperature, although this also reduces yield and increses the rate of catalyst deactivation.

2). Xylenes Plus

Xylene Plus also converts toluene with or without C_9^+ aromatic. Feed that have been comercially used include catalytic reformate and hydrotreated pygas. Catalyst is non noble metal. Hydrogen is not required for any facet (start-up, operation, catalyst

regeneration) of the process.,and thus operating pressure is relatively low. Reported that 30% per pass conversion result in highest possible yield of xylenes with minimal feedstock loss to gas or coke. EB production is close to zero.

3). Mobil's MTDP and STDP.

Mobil has developed several TDP processes. In the 1970s Mobil developed their LTD (Low Temperature Disproportionation) process. This was a liquid-phase process which used what described as siliceous zeolitic catalysts. Hydrogen was not required in this process. The initial reactor temperature was 127°C and was raised as the catalyst deactivated to maintain toluene conversion. Catalyst was regenarated after temperature reached about 315°C.

In the mid 1970s, Mobil introduced their MTDP process. This is vapor phase process that uses ZSM-5 type zeolites. The process operates at 48 wt% toluene per pass conversion with a near equlibrium PX selectivity of 24% in the xylenes product. Typical operating conditions are inlet temperature of 390-495°C, H_2 partial pressure of 4.1 Mpa, H_2/hydrocarbon molar ratio of 4, and liquid hourly space velocity (LHSV) = 1.0-2.0/h. EB production was about 3 wt% of feed.

In the late 190s, Mobil commercialized the MSTDP (Mobil Selective Toluene Disproportionation) proces. In MSTDP, PX selectivity can be boosted to 80-90% at toluene conversion of about 25-30%. The significantly higher than equilibrium yield of PX is obtained by precoking the catalyst in the reactor. As coking occurs, the toluene conversion progressively drops from 60% to about 20-30%, whereas the PX selectivity increases from 24% to about 80-90%. It means that the subsequent crystallization or adsorption PX recovery facilities can be significantly smaler. Typical operating condition are 400-470°C, 2.0-3.4 Mpa, WHSV= 2-4/h, H_2/hydrocarbon molar ratio of 1-3.1.

In the design chosen as selective toluene disproportonation because selectivity of paraxylene is higher at low conversion. It cause easier and cheeper in purification

2. METHODE

2.1. Kinetics Overview

The purpose is to determine effect of temperature (T) to reaction rate constant (k) in particular selective toluene disproportionation reaction. Reaction rate equation as follows:

$$-rA = k\ PA^2 \qquad .....(2.1)$$

Where :

PA: partial pressure reactant (atm)

k: reaction rate constants ($mol^{-1}hr^{-1}g\ cat^{-1}\ atm^{-1}$)

According to Arrhenius equation:

$k = ko\ e^{-E / RT}$

$$k=819.49 \exp (-65000/R.T) \qquad .....(2.2)$$

Where :

k = reaction speed constant, $kmol^{-1}hr^{-1}kg\ cat^{-1}\ atm^{-1}$

ko = Factor collision frequency, $kmol^{-1}hr^{-1}kg\ cat^{-1}\ atm^{-1}$

E = activation energy, kJ/kmol

R = universal gas constant, kJ/(kmol.K)

T = temperature, K

From Arrhenius equation above, reaction rate constant (k) is a function of temperature (T). higher temperature cause greater value of k. Therefore reaction take place on high temperature, but high temperature should be limited. When reaction temperature is high, there will be adverse reactions which hydrodealkisasi reaction of toluene into benzene and methane. Reaction will be decrease p-xylene conversion. Formation of CH_4 gas can contaminate the reaction proceeds so purity of product to be achieved is reduced.

2.2. Thermodynamics Overview

The purpose is to determine characteristic of reaction occurred in terms of heat of formation (ΔH°f) and to investigate whether reactions that occur in same direction or not in terms of Gibbs free energy (ΔG°f).

$\Delta H°_f$ standard = $\Delta H°_f$ product – $\Delta H°_f$ reactant

$\Delta H°_f$ = (-) exothermic reaction

$\Delta H°_f$ = (+) endotermic reaction

(Carl L Yaws, 1999)

For reaction occure at temperature 25°C :

ΔH^0_f standar = $\Delta H°_f$ product – $\Delta H°_f$ reactant

= ((133.3248) + ((0.947 x 68.0116)+(0.043 x 67.3116) + (0.01 x 69.1095))) – (2 x 50.2086)

= 100.9001 kj/mol

From calculation above, reaction takes place in endhotermic which is used heat.

For reaction occure at temperature 450°C:

$\Delta H°_f$ Reaction = $\Delta H°_f$ product – $\Delta H°_f$ reactant

= 67,645,843.800 – 67,069,069.920

= 576,773.880 kj/mol

Calculation for Gibbs Energy ($\Delta G°_f$):

$\Delta G°_f$ = (-) spontant

$\Delta G°_f$ = (+) not spontant (Carl L Yaws, 1999)

For reaction occure at temperature 25°C:

$\Delta G°_{f\ 298}$ = $\Delta G°_f$ product - $\Delta G°_f$ rektan

= (129.4076) + ((0.947 x 120.6964) + (0.043 x 118.4525) + (0.01 x 121.6905)) – (2 x 121.6636)

= -3.3445 kcal/mol

= -3,344.5 kcal/kmol

ln K = - $\Delta G°_f$ / (RT)

= 3,344.5 / (1,987 x 298)

= 5.482

K = 283.7802

Reaction occure at 723 K (450°C) :

$\Delta G°_{f\ 450}$ = $\Delta G°_f$ product - $\Delta G°_f$ reactant

= -15,414.3 kcal/mol

ln K = - $\Delta G°_f$ / (RT)

= 15,414.3 / (1.987 x 400)

= 19.3939

K = 264,645,036.2

Constant prices >>> 1 it is mean reaction that takes place is irreversible. Thus selective toluene disproportionation reaction is endothermic and Irreversible

2.3 Process Step

2.3.1. Raw Material Storage Stage

In this stage, raw materials is stored before it is used for production process. Toluene as raw material is stored in tank F-101 because it is in liquid form at T = 30°C and P = 1 atm. Hydrogen gas flowed through pipeline from plant with a pressure of 1 atm.

2.3.2. Preparation of Raw Materials Stage

This stage is intended to prepare raw material toluene and H_2 before fed to reactor. In accordance with operating conditions determination. This stage includes:

a. Changing Phases and Raising Pressure Toluene

Fresh toluene with purity of 99.9% wt is pumped from F-101 and mixed with toluene recycle derived from top stream of distillation column D-101 and xylene filtrate from centrifuge H-102 in mixing valve 1. Temperature of third stream reaches 87.98°C. From mixing valve 1 , mixture is then pumped to vaporizer (V-101) to change phase from liquid into gas at temperature of 111.37°C and pressure is increased from 1 atm to 8 atm with a centrifugal compressor G-101. Then, mix toluene is mixed with H_2 gas (H_2 make-up and H_2 recycle from gas-liquid separator H-101) in mixing valve 1. Operating

conditions of reactor at temperature of 450°C and a pressure of 30 atm, so that pressure is compressed again until 30 atm in G-104 and flow into furnace (Q-101) to raise its temperature up to 450°C. Toluene is ready fed to reactor (R-101).

b. Raising Pressure Hydrogen

Hydrogen gas is purchased from PT ALIndo Merak Banten streamed inline at 1 atm pressure and then compressed to 8 atm by a compressor G-103. H_2 make-up gas is mixed with H_2 recycle gas stream comes from gas-liquid separator (H-101) after pressure is raised from 1 to 8 atm by a compressor G-102.

2.3.3. Reaction Stage

Selective toluene disproportionation reaction occurs in reactor form paraxylene as main product and benzene as byproducts. The main raw material are toluene, hydrogen and solid catalyst zeolite ZSM-5. The reactor used is a multi tube fixed bed reactor to conduct gas-solid reactions. In which , gas phase are toluene and hydrogen while solid phase is zeolite ZSM-5 catalyst. The process takes place in non-isothermal adiabatic. Reaction temperature between 450-446°C and a pressure of 30 atm. The reaction is endothermic.

2.3.4. Separation and Purification Products Stage

Stream out of reactor in form of gas phase has temperature of 427°C and pressure at 30 atm. The heat is used to boil up water to produce steam, so temperature decrease to 227°C. Pressure is decreased to 2 atm with expander G-105 and condensed in condenser E-101 until temperature at 50°C. For process separation between hydrogen gas fraction with BTX liquid fraction (benzene, toluene, xylene), the stream is fed to gas-liquid separator (H-101). At T = 42.73°C and P = 1 atm. H_2 as non condensable fraction flow to top of separator as H_2 recycle while BTX as condensable fraction flow to bottom separator and pass through column distillation D-101 to separate benzene from mixture.

In column distillation D-101, benzene as distillate is obtained at temperature 80.46°C and P = 1 atm. Components in bottom stream (xylene and toluene) at temperature 118.62°C and pressure of 1.2 atm, then it is fed into distillation column D-102 to separate toluene from xylene. Top stream of D-102 is toluene at temperature 104.76°C and P = 1 atm is recycled and mixed with fresh feed toluene as feed reactor. Bottom stream of D-102 obtain mixed xylene at temperature of 154.8°C and pressure of 1.5 atm. Xylene is cooled gradually with heat exchanger E-107 and heat exchanger E-108 until T = 5°C then fed to crystalizer (E-109).

Crystalizer is used to separate paraxylene from xylene mixture based on differences in freezing point. Freezing point of paraxylene at temperature 13.26°C while ortho and metaxylene freezing point below -25°C therefore crystalizer operates at temperatures between 0-10°C with ammonia (NH_3) as refrigerant. The output of crystalizer obtain mixture of paraxylene crystals and liquid of meta and orthoxyelene. Paraxylene crystals is then separated in a centrifuge (H-102). Filtrate contain ortho and metaxylene is recycled as feed reactor for paraxylene whereas reisomerized, while crystals paraxylene is melted at temperature of 30°C in melter (Q-102) with water as heating medium (T = 30°C) in order to obtain paraxylene in a liquid phase with purity of 99.7% wt.

2.3.5. Products Storage Stage

Benzene obtained as top stream of D-102 is decreased its temperature to 30°C in cooler (E-104) and pumped into storage tank (F-102) in condition of T = 30°C and P = 1 atm. Paraxylene in liquid phase is pumped from melter to storage tank (T-03) in condition of T = 30°C and P = 1 atm . Both products are ready to market.

3. DISCUSSION

3.1 Equipment Spesification

Reactor

Code : R-120

Function	: reacting toluene and hydrogen as much as 293,172 kg/hr to produce xylene and benzene
Type	: fixed bed multitube
Operating condition	
- Pressure	: 30 atm
- Temperature	: 450°C
- Residence time	: 0.0242 second
Specifications of shell	
- IDS	: 61 in
- Thickness	: 5/16 in
- Baffle space	: 0.38 m
- Number of passes	: 1
- Material	: carbon steel SA 283 grade C
Specifications of tube	
- Number of tube	: 800
- BWG	: 16
- ID tube	: 1.37 in
- OD tube	: 1.5 in
- Pitch	: 1 7/8 in
- Composition	: triangular
- Material	: carbon steel SA 283 grade C
Reactor Diameter	: 1.7 m
Head shape	: torispherical dished head
Thickness of head	: 5/16 in
Head height	: 0.54 m
Total reactor height	: 3.69 m

3.2 Utilitas

Utility and laboratory units are important parts to support ongoing process in plant. Utility units includes units to provide water, steam, electricity, fuel and pressurized air.

3.3 Management

The established Paraxylenecompany has some following specifications:

a. Form of The Company : Limited Company
b. Industry : paraxylene plant
c. Company Location : Cilegon

3.4 Economic Analysis

In plant design required economic analysis to estimates amount of profit earned, length of investment capital can be restored, investment feasibility, and break-even point. Economic analysis is also used to determine if plant is to be established and be profitable or not feasible or not established.

4. CONCLUSION

Paraxylene plant is considered a high risk plant, it is caused by operating conditions at pressure of 30 atm and temperature of 450°C. The economic feasibility analysis of paraxylene plant is expressed as follows:

1. Profit before tax of Rp.436,271,324,400.45per year
   Profit after tax of Rp.327,203,493,300.34 per year.
2. ROI (Return On Investment) before taxes is 85.61%
   ROI (Return On Investment) after tax is 64.21%
   ROI (Return On Investment) before tax for high-risk plant is minimum 44% (Aries and Newton, 1995).
3. POT (Pay Out Time) before taxes is 1 years
   POT (Pay Out Time) after tax is 1.2 years
   POT (Pay Out Time) before tax for hgh-risk plant is maximum of 2 years (Aries and Newton, 1995).
4. BEP (Break Event Point) is 43.54%
   BEP for chemical plants generally range between 40-60%
5. SDP (Shut Down Point) is 27.5%.
   SDP for chemical plants generally range between 20-30%
6. DCF (Discounted Cash Flow) is 24.69%.

DCF acceptable is must be greater than interest on bank loans. The amount of DCF is minimum 1.5 times bank interest.

Based on results of economic feasibility analysis we concluded that paraxylene plant is feasible to build in Cilegon and deserves to be studied further.

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